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Infrared study of the valence transition compound $YbInCu_4$ using cleaved surfaces

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Optical reflectivity $[R(\omega)]$ of $YbInCu_4$ single crystals has been measured across its first order valence transition at $T_v \simeq 42$ K, using both polished and cleaved surfaces. $R(\omega)$ measured on cleaved surfaces $[R_c(\omega)]$ was found much lower than that on polished surface $[R_p(\omega)]$ over the entire infrared region. Upon cooling through T_v, $R_c(\omega)$ showed rapid changes over a temperature range of less than 2 K and showed only minor changes with further cooling. In contrast, $R_p(\omega)$ showed much more gradual and continuous changes across T_v, similar to previously reported data on polished surfaces. The present result on cleaved surfaces demonstrates that the microscopic electronic structures of $YbInCu_4$ indeed undergo sudden changes upon the valence transition, which is consistent with its first order nature. The gradual temperature evolution of $R_p(\omega)$ is most likely due to the compositional and/or Yb-In site disorders caused by polishing.

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Physical properties of strongly correlated "heavy fermion" compounds, most typically Ce-or Yb-based compounds containing a partly filled 4f shell, have attracted much attention.[1] The hybridization between the conduction (c) electrons and the otherwise localized f electrons leads to many interesting phenomena. Among them is a duality and crossover between itinerant and localized characters of the f electrons.[2] An important characteristic energy for the c-f hybridization is the Kondo temperature (T_K). At temperatures (T) well above T_K, f electrons are basically localized, resulting in local moment (Curie-Weiss) paramagnetism. With decreasing T, the c-f hybridization becomes progressively stronger. At $T \ll T_K$, the local moment is well-screened, and a spatially extended, coherent band is formed. Due to the strong Coulomb correlation of f electrons, the resulting bands show enhanced effective masses and a Pauli paramagnetism with a large effective moment. Associated with this crossover from localized to itinerant characteristics, the average valence of Ce or Yb ions deviates from 3 (decreases for Yb and increases for Ce).

Usually, such a T-induced crossover between localized and itinerant regimes is continuous, and marked by, e.g., a broad maximum in the T-dependence of susceptibility and/or the f electron-derived resistivity.[2] However, $YbInCu_4$ undergoes a first-order phase transition at $T_v \sim 42$ K between the high T phase (HTP) in a localized regime with $T_K = 20$ K and the low T phase (LTP) in an itinerant regime with $T_K = 300$ K.[3,4] Upon cooling through T_v, $YbInCu_4$ shows discrete changes in the lattice constant and many other physical properties. The Yb valence deduced from measured bulk thermodynamic properties is almost 3 in HTP, and about 2.9 in LTP. It is an intriguing question as to why this particular compound shows such a first-order transition between the two regimes, while most others show only continuous and gradual crossovers. Several models have been proposed as the origin for the transition.[5]

To understand the microscopic nature of such an electronic transition, it is important to probe the electronic structures around the Fermi level (E_F). For this purpose, infrared (IR) reflectivity $[R(\omega)]$ of $YbInCu_4$ has been measured in detail, at temperatures both above and below T_v.[6–9] $R(\omega)$ showed large changes between LTP and HTP. In the optical conductivity $\sigma(\omega)$ obtained from $R(\omega)$, a marked mid-IR peak was observed in LTP, which was interpreted[7] as arising from optical excitations in the c-f hybridized state.[10] This optical result demonstrated that the microscopic electronic structures around the Fermi level indeed undergo large changes upon the valence transition. However, the observed $R(\omega)$ seemed to show gradual variations upon cooling through T_v.[9] Such a T dependence is in contrast to the first-order nature of the transition.

Interesting results have been also reported concerning the Yb valence in $YbInCu_4$ studied by photoemission spectroscopy (PES).[11–13] In early PES studies on scraped surfaces with a vacuum UV source,[11] where the escape depth of photoelectrons was small, only a gradual change of valence was observed across T_v, and the valence was much lower than that given by the bulk properties. However, as the escape depth increased with soft and hard x-ray sources and as the sample was prepared by cleaving (fracturing), a much sharper change of valence was observed, and the valence was much closer to the bulk values.[12,13] These PES results strongly suggest that the valence and its transition in $YbInCu_4$ are extremely sensitive to disorder, caused either by scraping or by the presence of the surface itself.

Motivated by the above developments, we have measured infrared $R(\omega)$ of $YbInCu_4$ *using both polished and cleaved surfaces* of single crystals taken from the same batch, and have tried to obtain intrinsic $\sigma(\omega)$ of $YbInCu_4$. Although the $R(\omega)$ spectra measured on cleaved surfaces $[R_c(\omega)]$ had qualitatively similar spectral shapes to those on polished surfaces $[R_p(\omega)]$, the magnitude and T dependences were remarkably different between $R_c(\omega)$ and $R_p(\omega)$. With decreasing T, $R_c(\omega)$ showed sudden spectral changes at T_v, while $R_p(\omega)$ showed only gradual changes. The variations of $R_c(\omega)$ are very consistent with the first-order nature of the transition

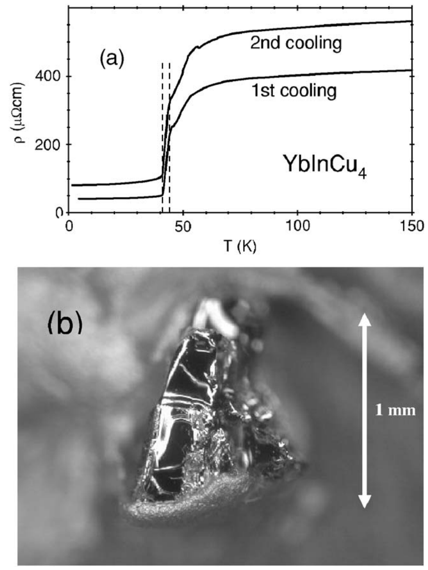

FIG. 1. (a) Resistivity (ρ) of YbInCu$_4$ single crystal as a function of temperature (T). Two vertical lines indicate 41 and 44 K. (b) Photograph of cleaved (fractured) surfaces of a YbInCu$_4$ single crystal. The dark areas indicate flat, specular surfaces.

and demonstrate that the microscopic electronic structures in YbInCu$_4$ indeed undergo a sudden change at T_v. We analyze the origin of gradual changes in $R_p(\omega)$ in terms of microscopic disorder caused by polishing.

The samples used in this work were single crystals grown by an In-Cu self-flux method, similarly to that previously described.[4] The resistivity of the single crystal decreased rapidly between 41 and 44 K, as shown in Fig. 1(a), consistent with the reported value of T_v=42 K. The higher resistivity of the second cooling cycle is also consistent with that reported previously.[4] This increase of resistivity after the first temperature cycle was attributed[4] to internal strain caused by the lattice contraction upon warming through T_v. To obtain cleaved surfaces, a block of single crystal was fractured into small pieces. They had flat, specular surfaces only with small dimensions (typically 50–500 μm). Those having such specular surfaces were mounted in a continuous-flow liquid He cryostat. The photograph of a measured sample is shown in Fig. 1(b). $R_c(\omega)$ spectra of thus mounted samples were measured using an IR microscope and an IR synchrotron radiation (SR) source at the beam line BL43IR of SPring-8.[14] Owing to the high brilliance of IR-SR, it was possible to focus the beam to a spot of ~15 μm diameter at the sample without using any aperture in the optical path. This enabled us to easily measure $R_c(\omega)$ of the small specular surfaces of YbInCu$_4$. To obtain $R_p(\omega)$, the crystals taken from the same batch as those used for $R_c(\omega)$ were mechanically polished. $R_p(\omega)$ were measured using an apparatus without a microscope, as previously described.[16] $R_p(\omega)$ were measured up to 30 eV using a SR source at the beam line BL7B of UVSOR, Institute for Molecular Science. $\sigma(\omega)$ spectra were obtained from the measured $R(\omega)$ spectra using the Kramers-Kronig relations.[17] Due to a technical restriction, $R_c(\omega)$ spectra were measured at 0.06–2 eV only, above which they were smoothly connected to $R_p(\omega)$. Below the measured range, $R_c(\omega)$ and $R_p(\omega)$ were extrapolated using the Hagen-Rubens relation.[17]

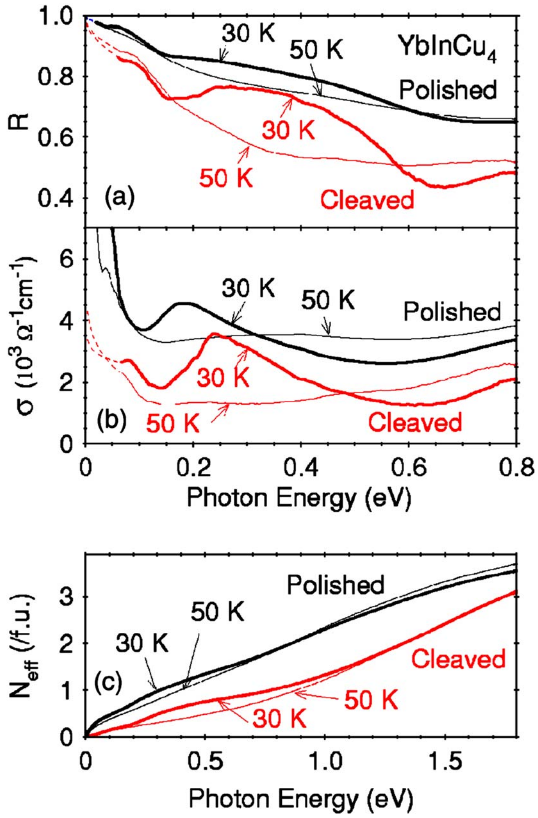

FIG. 2. (Color online) (a) Reflectivity spectra (R) of YbInCu$_4$ measured on cleaved and polished surfaces above and below T_v. (b) Optical conductivity spectra (σ) obtained from the reflectivity using the Kramers-Kronig relations. The spectra in the extrapolated region are indicated by broken curves. (c) Effective carrier density N_{eff} per formula unit (f.u.) calculated from $\sigma(\omega)$ using the optical sum rule.

Figure 2(a) shows $R_c(\omega)$ and $R_p(\omega)$ in HTP and LTP. The spectral shapes of $R_c(\omega)$ and $R_p(\omega)$ are qualitatively similar to each other. Namely, in the high-T phase the spectrum is a decreasing function of photon energy. In the low-T phase, on the other hand, the reflectivity at 0.2–0.55 eV increases significantly and shows a marked dip centered at ~0.15 eV. These spectral variations are qualitatively similar to previous results.[7–9] However, the over all magnitude of $R_c(\omega)$ is much lower than that of $R_p(\omega)$. We have carefully confirmed that the low value of $R_c(\omega)$ is not due to experimental errors, but an intrinsic property of the cleaved surfaces.[15] In addition, the difference in $R_c(\omega)$ between the two phases is much larger than that in $R_p(\omega)$. Figure 2(b) shows the optical conductivity spectra of the cleaved $[\sigma_c(\omega)]$ and polished $[\sigma_p(\omega)]$ samples, obtained from $R_c(\omega)$ and $R_p(\omega)$, respectively. They show a large difference in their magnitude, corresponding to that between $R_c(\omega)$ and $R_p(\omega)$, while their spectral shapes appear qualitatively similar to each other. It appears as though $\sigma_p(\omega)$ results from the superposition of a constant background upon $\sigma_c(\omega)$. Note, however, that the mid-IR peak energy of 0.25 eV in $\sigma_c(\omega)$ is about 70 meV higher than in $\sigma_p(\omega)$. In previous works on polished samples, the

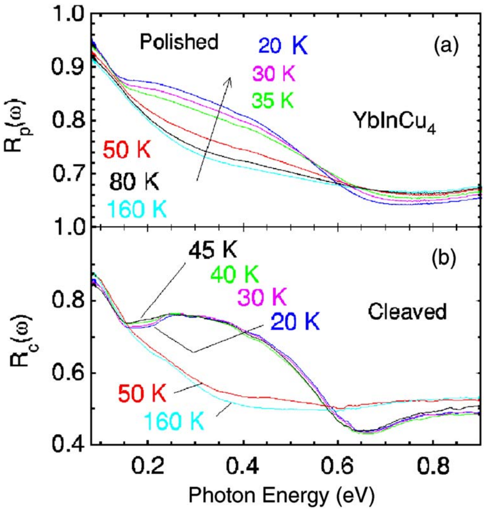

FIG. 3. (Color online) Reflectivity spectra of YbInCu$_4$ single crystals measured on (a) polished and (b) cleaved surfaces. Note that the vertical scale is different between (a) and (b).

mid-IR peak in $\sigma(\omega)$ was centered at $\sim$0.25 eV,[8,9] and at $\sim$0.3 eV ($\sim$2500 cm^{-1}).[7] Figure 2(c) shows the effective carrier density $N_{\text{eff}}(\omega)=(2m_0/\pi e^2)\int_0^{\omega}\sigma(\omega')d\omega'$ given by the optical sum rule.[17] The sum rule is satisfied (the spectral weight transfer is completed) at 1.3 eV for the cleaved sample, since N_{eff} below T_v is almost equal to that above T_v for $\hbar\omega \geqslant 1.3$ eV. In contrast, it is not satisfied up to 1.8 eV for the polished sample.

Figure 3 compares the detailed T dependences of $R_c(\omega)$ and $R_p(\omega)$. $R_p(\omega)$ changes gradually with decreasing T, and keeps changing even below 40 K. These spectral evolutions agree well with those previously reported for polished surfaces.[9] The $R_c(\omega)$ spectra, on the other hand, show large changes over a very narrow T range. In addition, $R_c(w)$ is almost unchanged in LTP, with only minor variations in the shape of the dip. Clearly, the T-dependence of $R_c(\omega)$ is quite different from that of $R_p(\omega)$. In Fig. 4, to show their T variations more quantitatively, $R_c(\omega)$ and $R_p(\omega)$ integrated at 0.2–0.55 eV are plotted as a function of T. It is seen that the change in $R_c(\omega)$ occurs at $\sim$46 K over a T range of less than 2 K, in contrast to the gradual change of $R_c(\omega)$.[18] While the T variation in $R_c(\omega)$ is as sharp as that in the resistivity, the transition T of 46 K implied by $R_c(\omega)$ is slightly higher than 41–44 K implied by the resistivity [Fig. 1(a)]. The variations of integrated $R_c(\omega)$ with T was accompanied by a hysteresis of about 1 K. Such a hysteresis is consistent with those observed in the thermodynamic properties. Another interesting feature in Fig. 4 is that no significant difference is observed in $R_c(\omega)$ between the first and second cooling cycles, in contrast to the different resistivities for the first and second coolings [see Fig. 1(a)].

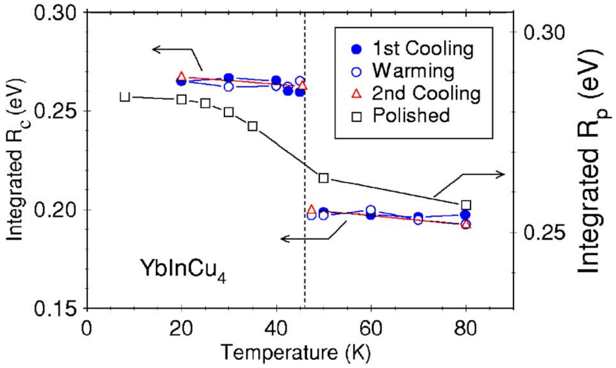

FIG. 4. (Color online) $R_c(\omega)$ and $R_p(\omega)$ integrated from 0.2 to 0.55 eV as a function of temperature. The vertical line is drawn at 46 K and is a guide to the eye.

Clearly, the T evolution of $R_c(\omega)$ is more consistent with the first-order nature of the valence transition, and with the T variations of other physical properties such as resistivity and susceptibility, which change suddenly upon the transition and remain almost constant below T_v. Hence the $R_c(\omega)$ data should reflect the intrinsic bulk electronic structures of YbInCu$_4$ more closely and directly than the $R_p(\omega)$ data. However, as mentioned before, the spectral shape of $\sigma_c(\omega)$, in particular the mid-IR peak in LTP, is qualitatively similar to that in $\sigma_p(\omega)$. Hence the interpretation of $\sigma(\omega)$ in LTP in terms of a c-f hybridized state reported in the previous works[7–9] should remain valid. The origin for the spread of mid-IR peak energies (0.18–0.3 eV) for polished samples in this work and in the previous works[7,8] is unclear. It may have resulted from differences in the specific way the polishing was done in these works. On the other hand, the magnitude and T-dependence of $\sigma_c(\omega)$ are quite different from those of $\sigma_p(\omega)$. Therefore the previous data on the spectral weight and its T-induced transfer in $\sigma(\omega)$ measured for polished YbInCu$_4$ should be interpreted carefully.[7,9]

The broadened T dependence in $R_p(\omega)$ should be due to disorder introduced by the mechanical polishing. Two kinds of disorder are likely to be responsible: a deviation from the ideal 114 composition and a site disorder. Since the early stage of research on YbInCu$_4$, it has been recognized that the T_v value for Yb$_{1-x}$In$_{1+x}$Cu$_4$ is a sensitive function of x.[3] Such a compositional disorder is quite likely to result from mechanical polishing, which may lead to a distribution of T_v within the penetration depth of the IR radiation. The penetration depth of YbInCu$_4$ in the photon energy range of 0.1 to 0.2 eV has been estimated to be 500–1000 Å from the absorption coefficient obtained with the Kramers-Kronig analysis of $R_c(\omega)$ and $R_p(\omega)$. In addition, even in high-quality YbInCu$_4$ samples with a negligible compositional deviation, a site disorder tends to occur between the In and Yb sites (Yb occupying In site, and vice versa).[19] It has been pointed out that such a site disorder may change the Yb valence and the T_v value.[19] It is likely that the surface layer of a mechanically polished sample has more site disorder, and hence a broader transition, than that of a cleaved surface. We believe that the broadened T variation of $R_p(\omega)$ results from the compositional and/or site disorder.

Note that the sudden change of $R_c(\omega)$ occurs at 46 K, in contrast to 41–44 K in the resistivity. This is a rather unexpected result, since it is natural to expect $R(\omega)$ and resistivity to change at the same transition temperature. The origin for this difference is unclear at the present time. One possibility is that T_v is sensitive even to the cleaving, so that the T_v becomes slightly higher at the near-surface region [without, however, a distribution of T_v since the T variation of $R_c(\omega)$ itself is very sharp]. Further study is needed to clarify this point.

In addition to the different T dependences, $R_c(\omega)$ has much lower magnitude than $R_p(\omega)$ at all measured T's, as mentioned above. Since the higher $R_p(\omega)$ has been caused by polishing, it is also likely due to disorder. The higher $R_p(\omega)$ probably results from higher reflectivity of the composition-disordered or site-disordered portion of $YbInCu_4$ in the surface layer. It is even likely that some fraction of the disordered portion at the surface does not undergo the valence transition, hence contributing a T-independent, constant background in $R(\omega)$ and $\sigma(\omega)$.

In conclusion, IR reflectivity spectra of $YbInCu_4$ have been measured on cleaved and polished surfaces of single crystals. The reflectivity spectrum measured on the cleaved surface showed sudden changes over a narrow T range upon the valence transition, in contrast to the gradual T evolution observed for polished surfaces. The result on the cleaved surface demonstrates that the microscopic electronic structures in $YbInCu_4$ indeed undergo a first-order transition. The broadened T evolution of reflectivity for the polished sample has been analyzed in terms of compositional and/or Yb-In site disorder caused by polishing.

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